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Platinum–Alumina Interaction in the Electron Microscope

In the course of electron microscopy work involving the observation of small platinum metal particles supported on a thin film of γ-alumina a reaction was observed between the platinum particles and the support when a sufficiently high flux of electrons was used to irradiate the specimen. The latter was prepared as follows: γ-alumina film of about 100 Å thickness was deposited by Rf sputtering onto a quartz glass slide and a layer of 10 Å of platinum was deposited on top of the γ-alumina in the same way. This quartz slide was subsequently heat-treated at 100°C for 50 hr in an enclosed oxygen atmosphere, after which the alumina film containing platinum particles was stripped from the quartz support and carbon-coated to eliminate charging in subsequent transmission electron microscope examination in a Philips EM 300 at 100 kV.

Due to the heat evolved by absorption of a purposely intense electron beam (typically 15 μA beam current, beam diameter of 3000 Å) the larger opaque platinum particles, which originally had displayed sharp edges typical of crystalline bodies, were found to melt and form spherical particles that started to move on the substrate, in which process they were seen to consume the alumina film. Platinum particles smaller than 0.1 μm were unaffected by the beam.

After a certain length of exposure to the high-intensity beam, which varied from case to case and was of the order of minutes, a drop of molten material was seen to interact with the support alumina forming a dark-appearing compound whose single-crystal character was determined by electron diffraction in the microscope. This interaction involved transfer of platinum or possibly platinum–aluminum alloy from the molten drop into the adjacent alumina substrate in a process that resembled the motion of water being absorbed by paper tissue owing to capillary forces. The molten state of the original platinum particle does not seem to be a prerequisite, however, for the reaction to take place. At times the reaction was observed to proceed while the platinum particle remained apparently in the solid state. It is believed that reactions of this type could be linked to and shed light on the mechanism of aging and loss of activity of some platinum-based catalyst systems.

Figure 1 is an electron micrograph showing an opaque particle of presumably Pt–Al alloy (A), with neighboring dark compound formed by the reaction with the substrate (B), neighboring unaltered γ-alumina substrate (C), and carbon support film (D).

Energy dispersive X-ray analysis of this compound in the electron microscope using a Li-drifted silicon crystal Kevex energy dispersive detector and a Northern Scientific 750 multichannel analyzer proved the presence of platinum and aluminum, while oxygen, if present, could not be revealed. Selected-area electron diffraction patterns of the compound were taken at various angles of tilt of the specimen stage.

Figure 2 shows the diffraction pattern obtained from the dark compound (area B in Fig. 1) with the (100) lattice plane normal to the electron beam. Calibration of the instrument constant for determining

FIG. 1. Electron micrograph of a single-crystal compound (B) formed by interaction of Pt–Al alloy (A) with alumina substrate (C).

the lattice plane spacings was provided by the γ-alumina original support whose diffraction rings are visible in Fig. 2. Electron diffraction patterns were exposed at low electron currents to avoid specimen heating and its possible effect on the measured lattice parameters. In this way a high accuracy of calibration could be obtained. Figure 2 and other diffraction patterns obtained from the dark compound with

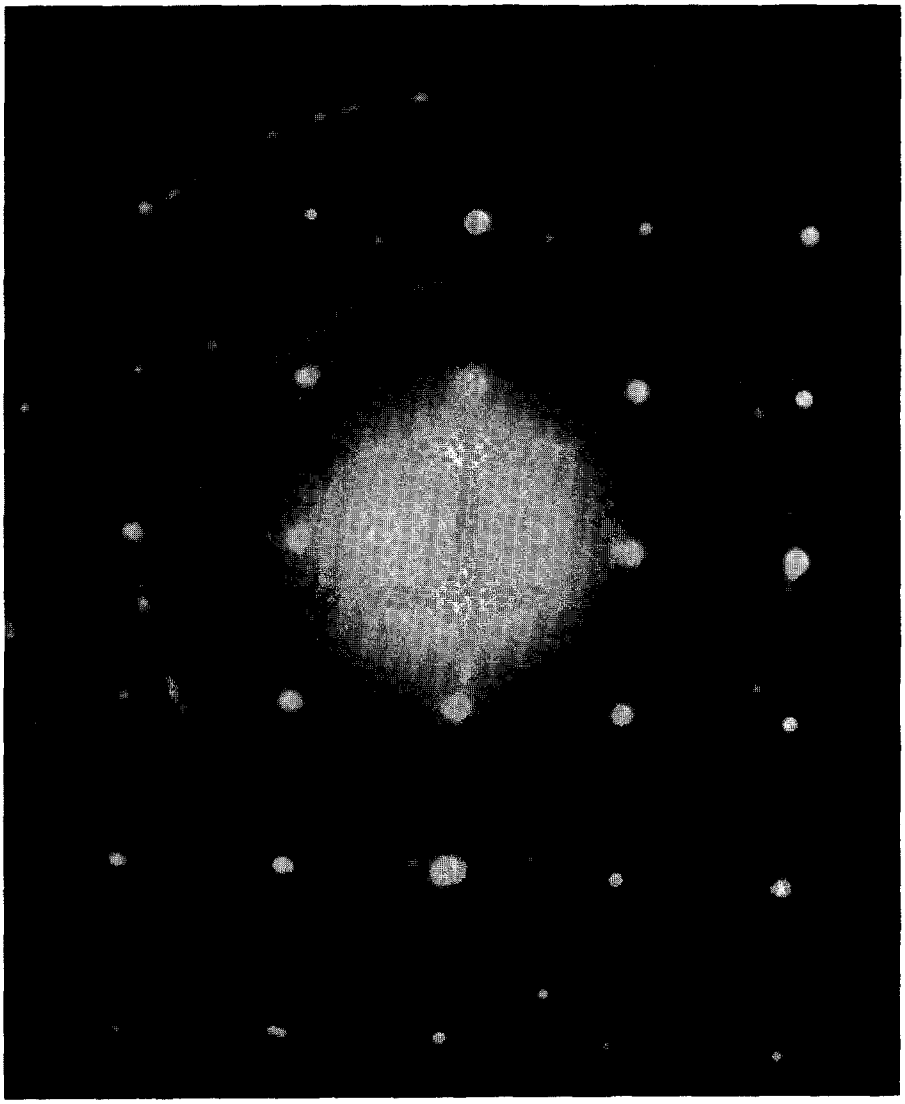

FIG. 2. Electron diffraction pattern (100 plane) of the Pt_3Al compound.

varying degrees of stage tilt were all interpreted as consistent with a primitive cubic lattice cell with $a = 3.88$ Å.

The diffraction data agree well with those of Pt_3Al as determined by Huch and Klemm (*1*) ($a = 3.876$ Å, space group $Pm3m$, structure as in Cu_3Au). The formation of Pt_3Al by a reaction of platinum metal above its melting point with γ-alumina in the beam of the electron microscope is a close analog to the formation of Pt–Al intermetallic compounds from Al_2O_3 and Pt in reducing atmosphere (ammonia) described in the literature (*2,3*). A corrosive reaction of Pt with alumina at temperatures above 1200°C also was reported in inert gas (argon) and in vacuum (*4*).

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J. W. SPRYS
Z. MENCIK

Scientific Research Staff
Ford Motor Company
Dearborn, Michigan 48121
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